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We investigate the Josephson effect through a molecular quantum dot magnet connected to superconducting leads. The molecule contains a magnetic atom, whose spin is assumed to be isotropic. It is coupled to the electron spin on the dot via exchange coupling. Using the numerical renormalization group method we calculate the Andreev levels and the supercurrent and examine intertwined effect of the exchange coupling, Kondo correlation, and superconductivity on the current. Exchange coupling typically suppresses the Kondo correlation so that the system undergoes a phase transition from 0 to π state as the modulus of exchange coupling increases. Antiferromagnetic coupling is found to drive exotic transitions: the reentrance to the π state for a small superconducting gap and the restoration of 0 state for large antiferromagnetic exchange coupling. We suggest that the asymmetric dependence of supercurrent on the exchange coupling could be used as to detect its sign in experiments.

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Molecular spintronics [1] aims at exploring spin-dependent electronic transport through molecules with intrinsic degrees of freedom such as spin, connected to leads of various nature. On the theoretical and experimental side, recent advances have concerned both coherent [2] and incoherent [3, 4, 5] transport through these molecular quantum dot magnets (MQDM). They consist of a magnetic molecule with either a large [6] or a small anisotropy, as is the case for a endofullerene molecule [7].

Here, we provide a nonperturbative computation of the low temperature transport properties of a MQDM connected to superconducting leads using a numeral renormalization group (NRG) approach. The Josephson current allows a diagnosis of the interaction between the intrinsic spin of the molecule, its itinerant electron spin, and the polarization of the leads. It has been known for some time [8, 9, 10, 11], and recently analyzed in experiments [12], that a quantum dot sandwiched between superconducting leads can show a π junction behavior [13]. At the same time, a quantum dot connected to leads at low enough temperatures exhibits the Kondo effect [14]. It was shown [9, 15, 16] that with superconducting leads, at low temperature the 0 junction state of the Josephson current is restored when the Kondo temperature exceeds the superconducting gap. The stability of this Kondo phase is put in question in the presence of additional spin degrees for freedom [17] which may compete with Kondo screening. Here the Josephson current flows through an isotropic MQDM which can describe a endofullerene molecule [18]. The electron spin in the quantum dot and the magnetic ion inside it interact via an exchange coupling [4]. We calculate the Andreev level (AL) spectrum and the supercurrent and determine the spin of the ground state. We find that the exchange coupling typically suppresses the Kondo effect and drives a transition from 0 to π state. Moreover, antiferromagnetic coupling is found to drive exotic transitions: the reentrance to π state for small superconducting gap and the restoration of 0 state for large J.

The MQDM connected to two s-wave superconducting leads (inset of Fig. 1) is modeled by a single-impurity Anderson model: $\mathcal{H} = \mathcal{H}_{\rm M} + \mathcal{H}_{\rm L} + \mathcal{H}_{\rm T}$, where

$$\mathcal{H}_{\rm M} = \epsilon_0 n + U n_\uparrow n_\downarrow + J\mathbf{S}\cdot\mathbf{S}_{\rm e} \tag{1}$$

$$\mathcal{H}_{\rm L} = \sum_{\ell\mathbf{k}} \left[\epsilon_{\mathbf{k}} n_{\ell\mathbf{k}} - \left(\Delta\, e^{i\phi_\ell} c^\dagger_{\ell\mathbf{k}\uparrow} c^\dagger_{\ell-\mathbf{k}\downarrow} + (h.c.)\right)\right] \tag{2}$$

$$\mathcal{H}_{\rm T} = \sum_{\ell\mathbf{k}\mu} \left[t\, d^\dagger_\mu c_{\ell\mathbf{k}\mu} + (h.c.)\right]. \tag{3}$$

Here $c_{\ell\mathbf{k}\mu}$ (d_μ) destroys an electron with energy $\epsilon_{\mathbf{k}}$, and spin μ on lead $\ell = L, R$ (on the carbon cell); $n_{\ell\mathbf{k}}$ and n are occupation operators for the leads and the cell. The single-particle energy ϵ_0 can be tuned by gate voltages. J denotes the exchange energy between the ion spin $\mathbf{S}$ and the electron spin $\mathbf{S}_{\rm e} = \frac{1}{2}\sum_{\mu\mu'} d^\dagger_\mu \boldsymbol{\sigma}_{\mu\mu'} d_{\mu'}$. Δ is the superconducting gap. Except for the finite phase difference $\phi = \phi_L - \phi_R$, the leads are identical and their coupling to the MQDM is symmetric. The hybridization between the molecule and the leads is well characterized by a tunneling rate $\Gamma = \pi\rho_0|t|^2$, where ρ_0 is the density of states of the leads at the Fermi energy. As we are interested in the low temperature behavior, we concentrate for the most part on the Kondo regime with a localized level $-\epsilon_0 \gg \Gamma$ with large charging energy $U \gg |\epsilon_0|$. Specifically, we choose $\epsilon_0 = -0.1D$ (the band width D is taken as a unit of energy), $\Gamma = 0.01D$, and $U = \infty$ and introduce the bare Kondo temperature $T_K^0 = \sqrt{D\Gamma/2}\exp\left[\frac{\pi\epsilon_0}{2\Gamma}\left(1+\frac{\epsilon_0}{U}\right)\right]$ (at $J = \Delta = 0$). The energy spectrum is found with the NRG method [19] extended to superconducting leads [15, 20]. Within the NRG method, the supercurrent is directly obtained by evaluating the expectation value of the current operator [15].

Fig. 1 shows the phase diagram of our system, which constitutes the main result. The junction property

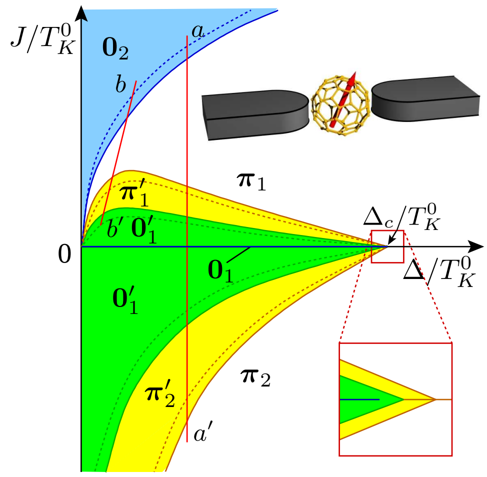

FIG. 1: (color online) Schematic phase diagram of a MQDM superconducting junction system [see the upper inset] indicating the 0, 0' (blue), π' (green), and π regions. Each region is divided into two subregions according to the ground-state spin: S and $S-1/2$ for $0_1^{(\prime)}$ and 0_2 regions and $S-1/2$ and $S+1/2$ for $\pi_1^{(\prime)}$ and $\pi_2^{(\prime)}$ regions, respectively. Note that the 0_1 state exists only along the line $J=0$ [see the lower inset]. For larger molecular spin $S'>S$ (see the dotted lines), the phase boundaries between 0_1 and $\pi_{1/2}$ are shifted toward smaller $|J|$, and one between 0_2 and π_1 moves toward larger J.

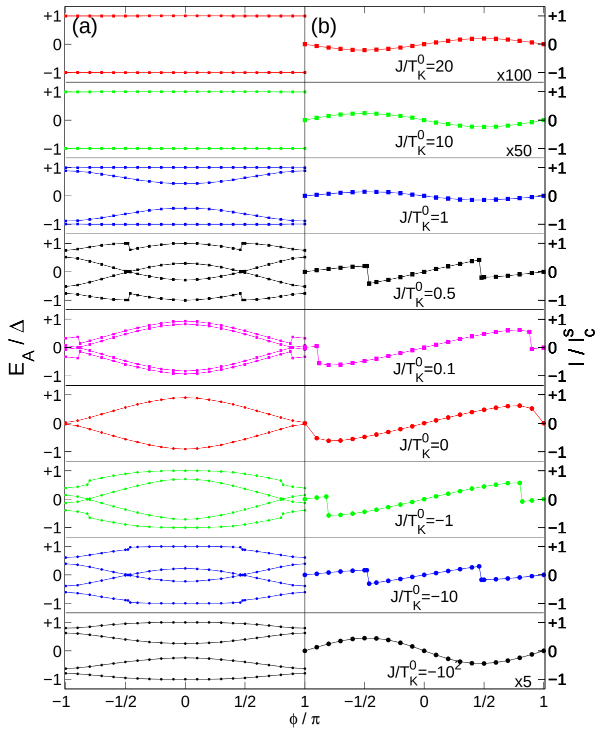

FIG. 2: (color online) (a) ALs in units of Δ and (b) supercurrents I in units of $I_c^s \equiv e\Delta/\hbar$ as functions of ϕ in the strong coupling limit ($\Delta/T_K^0 = 0.1$) for various values of J/T_K^0: see the line aa' in Fig. 1. Here the ion spin S is set to 1/2.

switches between 0 and π state, depending on the strengths of J and Δ with respect to T_K^0. For $J = 0$, the system undergoes the Kondo-driven phase transition [9, 15, 16]: The ground-state wave function is of spin singlet kind for $\Delta < \Delta_c \approx 1.84\,T_K^0$ and of spin doublet for $\Delta > \Delta_c$. In the strong coupling limit ($\Delta < \Delta_c$) Kondo correlations screen out the localized spin and Cooper pairs tunnel through the Kondo resonance state, resulting in a 0-junction [15, 16]. In the weak coupling limit ($\Delta > \Delta_c$), strong superconductivity in the leads leaves the local spin unscreened and the tunneling of Cooper pairs subject to strong Coulomb interaction acquires an additional phase π, making a π-junction [8, 9, 10, 15, 16]. It is also found [15] that the transition is ϕ-dependent so that a narrow region of the intermediate states $0'$ and π' exists; see the enlarged view in Fig. 1.

Finite exchange coupling between electron spins and the ion spin introduces another electronic correlation and affects Cooper pair transport. Fig. 2 shows typical variations of ALs and supercurrents with J along the line aa' (see Fig. 1) in the strong coupling limit ($\Delta/T_K^0 = 0.1$). Any finite J clearly induces a splitting in subgap excitations and consequently causes a crossing between the ground state and the lowest excitation at $\phi \neq \pi$ (at least for $|J/T_K^0| \lesssim O(1)$); the level crossing otherwise takes place only at $\phi = \pi$. Across the crossing, the ground state spin is changed from S to $S\mp 1/2$ for $J \gtrless 0$. Similarly, the ALs defined as the one-electron/hole subgap excitations (identified as the poles of the dot Green's functions [21]) exhibit discontinuities like kinks in the spectra; for $J \gtrless 0$ two outmost ALs with spin $S\pm 1/2$ with respect to the spin-S ground state cannot remain as (spin-1/2) one-electron excitations with respect to the ground state with spin $S\mp 1/2$ at the transition and are replaced by new ALs with spin $S\mp 1$. In parallel with an abrupt change in ALs, the supercurrent-phase relation (SPR) shows a discontinuous sign change (note that $I \propto -\partial E_A/\partial\phi$, as the continuum-excitation contribution is negligible [21]), culminating in a transition from 0 to π state: two $\pi^{(\prime)}$ states labeled as $\pi_{1,2}^{(\prime)}$ are identified according to the ground-state spin $S \mp 1/2$, respectively. The intermediate states $0_1'$ and $\pi_{1/2}'$ are defined as in Ref. [11]. The full 0 state exists only at $J = 0$ because any small J drives the system to the π state at $\phi = \pi$; see Fig. 2. The curve of $I(\phi)$ then has three distinct segments [15]. The central segment resembles that of a short ballistic junction, while the two surrounding segments are parts of π-junction curve. As J grows in magnitude the central segment shrinks and eventually vanishes. The SPR then becomes sinusoidal like in a tunnel junction. It should be noted that the 0-π transition is asymmetric with respect to the sign of J: the transition for $J > 0$ takes place at $\delta E_S \sim T_K^0$, where $\delta E_S = \frac{J}{2}(2S+1)$ is the exchange-coupling energy gap, while the 0 state survives much larger ferromagnetic coupling ($J < 0$). Once the π-

junction is fully established, stronger ferromagnetic coupling does not lead to any qualitative change in the SPR, while a second transition back to 0 state is observed for large antiferromagnetic coupling ($J \gg \Delta$). The NRG results distinguish the second 0 state (0_2) from the former one (0_1) in three points: (1) the ground state has spin $S-1/2$ like the π_1 phase, (2) the SPR is that of a tunneling junction, and (3) the π_1-0_2 transition has no intermediate state. Figure 3 (c) shows that the critical current has its maximum at $J=0$ and decreases with increasing $|J|$ rapidly across the phase boundary for $J>0$ or rather gradually for $J<0$. The critical current totally vanishes at the π_1-0_2 boundary and increases again slowly with J in 0_2 phase (see the curve for $\Delta/T_K^0 = 0.01$).

The 0-π transitions (0_1-π_1 and 0_1-π_2) can be attributed to the competition between superconducting and Kondo correlations as in the absence of exchange coupling. The relevant parameters are then the Kondo temperature T_K and the superconducting gap Δ, and the 0-π phase transition occurs when they are comparable to each other: In our choice of parameters the transition happens at $\Delta_c/T_K \approx 1.84$. The exchange coupling manifests itself by renormalizing the Kondo temperature $T_K(J)$. To see this, we applied the poor man's scaling theory to a corresponding Kondo Hamiltonian with no superconductivity and $S=1/2$: $\mathcal{H}_{\rm KM} = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} n_{\mathbf{k}} + J\mathbf{S}\cdot\mathbf{S}_{\rm e} + (J_{\rm K}\mathbf{S}_{\rm e} + J_{\rm M}\mathbf{S})\cdot\mathbf{S}_{\rm L}$, where $\mathbf{S}_{\rm L}$ is the spin operator for the lead electrons at molecule site. The last term $\mathbf{S}\cdot\mathbf{S}_{\rm L}$ describing direct coupling between spins of the ion and the lead electrons arises during the scaling process. The renormalization group analysis leads to the following scaling equations: together with $J \approx J(\Lambda = D)$,

$$\frac{dJ_{\rm K/M}}{d\ln\Lambda} \approx -\rho_0 J_{\rm K/M}^2 + \frac{J}{4D}(2J_{\rm K}J_{\rm M} - J_{\rm M/K}^2) \ . \quad (4)$$

As the band width Λ is decreased from D to T_K, the coefficient $J_{\rm K}$, responsible for the Kondo correlation, diverges and the scaling breaks down. In the presence of finite exchange coupling, however, since $JJ_{\rm K}J_{\rm M} > 0$ with $J_{\rm M}(\Lambda = D) = 0$ and $|J_{\rm M}| \ll J_{\rm K}$, the term proportional to J in Eq. (4) turns out to slow down the flow of $J_{\rm K}$ and accordingly lowers the Kondo temperature. This point is confirmed by NRG calculations applied in the absence of superconductivity. As can be seen in Fig. 3 (a) and (b), the width of the spectral density for dot electrons, identified as the Kondo temperature $T_K(J)$, decreases with increasing $|J|$ (for $J<0$ this decrease, being marginal, is not clearly shown with the logarithmic scale). We find out that for the ferromagnetic case the ratio $T_K(J)/T_K^0$ coincides with $\Delta_c(J)/\Delta_c(J=0)$. For the antiferromagnetic case, the Kondo correlation is observed to be suppressed not only by the Kondo peak narrowing but by lowering the peak height.

Antiferromagnetic exchange coupling can, on the other hand, exert a more profound effect than simply renormalizing the Kondo temperature: it gives rise to a reentrant

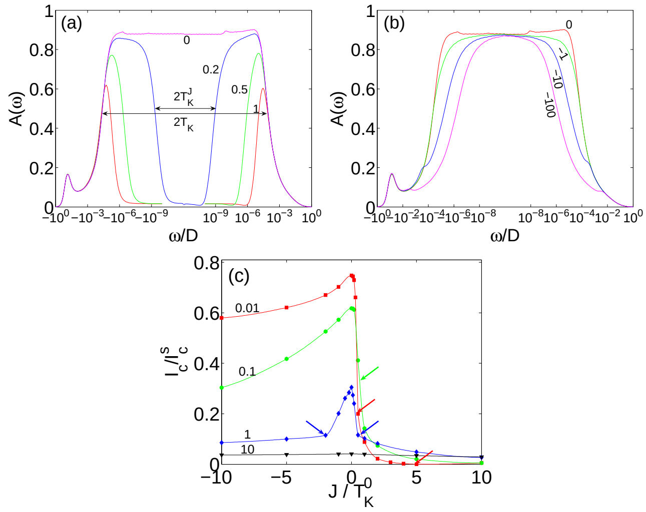

FIG. 3: (color online) Spectral weights $\mathcal{A}(\omega)$ for dot electrons coupled to normal leads with antiferromagnetic [(a)] and ferromagnetic [(b)] exchange coupling to ion spin for various values of J/T_K^0 (as annotated). (c) Critical currents as functions of J/T_K^0 for different values of Δ/T_K^0 (see the annotations). The arrows locate transition points corresponding to data with the same color. Here we have used $S=1/2$.

transition to the π state at small Δ and restoration of the 0 state for large J. It is known that small antiferromagnetic exchange coupling ($J \lesssim T_K^0$), studied in the context of coupled impurities [22] and side-coupled quantum dot systems [23] and observed in experiments [24], can produce a two-stage Kondo effect. After the magnetic moment of the dot is screened by conduction electrons below T_K, at a much lower energy scale (denoted as T_K^J) the ion spin is screened by the local Fermi liquid that is formed on the dot. T_K^J is then the Kondo temperature of a magnetic moment screened by electrons of a bandwidth $\sim T_K$ and density of states $\sim 1/(\pi T_K)$ [23]: $T_K^J \sim T_K \exp\left[-\frac{\pi T_K}{J}\right]$. The second Kondo effect leads to a Fano resonance and makes a dip in the dot electron density of states as shown in Fig. 3 (a). The dip becomes widened with J and overrides the Kondo peak when $T_K^J \approx T_K$ so that the Kondo effect is completely overridden. As long as $\Delta > T_K^J$, the second Kondo effect does not appear since the superconducting gap blocks any quasi-particle excitation with energy less than Δ. For $\Delta \lesssim T_K^J$, however, Cooper pairs notice the suppression of the Kondo resonance level, and their tunneling is governed by cotunneling under strong Coulomb interaction, forming a π-junction again. Since T_K^J decreases with decreasing J, Δ_c decreases to zero as $J \to 0$. Note that the extremely small $T_K^J \ll T_K$ (unless $\delta E_{\rm S} \sim T_K^0$) might make it hard to detect the reentrance even under rather weak thermal fluctuations with $T_K > T > T_K^J$.

The revival of the 0-state for strong antiferromagnetic coupling can be explained in the picture of cotunneling of Cooper pairs [10]. In weak coupling limit, the fourth-

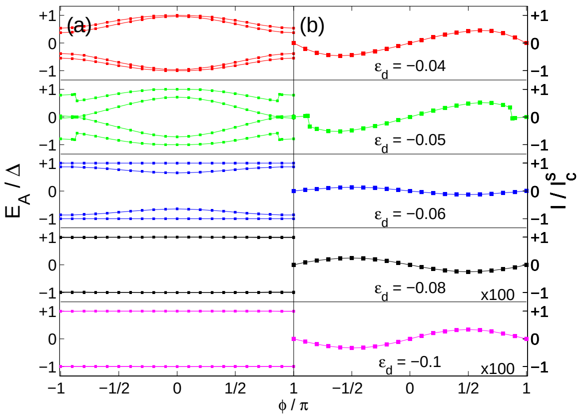

FIG. 4: (color online) (a) ALs in units of Δ and (b) supercurrents I in units of I_c^s as functions of ϕ with $J/T_K^0 = 10$ and $\Delta/T_K^0 = 0.02$ (at $\epsilon_d = -0.1$) while the gate voltage ϵ_d is tuned from -0.1 to -0.04. See the line bb' in Fig. 1.

order perturbation theory leads to the supercurrent:

$$I = \frac{4e}{\hbar}\sin\phi \sum_{\mathbf{k}\mathbf{k}'} t_{\mathrm{L}}^2 t_{\mathrm{R}}^2 \frac{u_{\mathbf{k}}u_{\mathbf{k}'}v_{\mathbf{k}}v_{\mathbf{k}'}}{\mathcal{E}_{\mathbf{k}}\mathcal{E}_{\mathbf{k}'}} \times \frac{1}{2S+1}\left(\frac{1}{E_{\mathbf{k}}+E_{\mathbf{k}'}} - \frac{2S+2}{\delta E_{\mathrm{S}}+E_{\mathbf{k}}+E_{\mathbf{k}'}}\right), \tag{5}$$

where $E_{\mathbf{k}} = \sqrt{\Delta^2+\epsilon_{\mathbf{k}}^2}$, $u_{\mathbf{k}} = \sqrt{(1+\epsilon_{\mathbf{k}}/E_{\mathbf{k}})/2}$, $v_{\mathbf{k}} = \sqrt{(1-\epsilon_{\mathbf{k}}/E_{\mathbf{k}})/2}$, and $\mathcal{E}_{\mathbf{k}} = -\epsilon_d - \frac{J}{2}(S+1) - E_{\mathbf{k}} < 0$. For antiferromagnetic coupling, the ground state for the uncoupled system has spin $S-1/2$. After one electron tunnels through the molecule the system can be in spin eigenstate of either $S-1/2$ and $S+1/2$. The latter virtual process, costing more energy by the gap δE_{S}, turns out to acquire a π phase, contributing to a negative supercurrent. The larger amplitude of this process by a factor $2S+2$ (degeneracy of the spin state $S+1/2$) dominates over spin-preserving process as long as the gap δE_{S} is small. For a large gap δE_{S}, however, this process becomes negligible and the sign of the supercurrent is reversed. Note that according to Eq. (5) the SPR is always sinusoidal and the current should vanish at the transition, which is also confirmed in our NRG calculations.

The physical arguments for the 0-π transitions discussed so far are valid for arbitrary values of the ion spin S, while the phase boundaries are shifted with changing S as shown in Fig. 1. The exchange-coupling energy gap δE_{S} that is supposed to compete with T_K increases with S so that for larger S the transitions can occur at smaller J. On the other hand, we have observed that the π_1-0_2 transition takes place at slightly larger J for larger S. This is because the increase in the degeneracy factor $2S+2$ overwhelms the decrease in matrix elements due to a larger energy cost by δE_{S} [see Eq. (5)].

Finally, we present potential experimental manifestations of exchange-coupling-driven 0-π transition. While the direct control of exchange coupling in molecules is difficult to achieve, the relative strength J/T_K^0 can be controlled by the gate voltage which can tune the Kondo temperature. Fig. 4 proposes a possibility to observe a double transition (along the line bb' in Fig. 1) as the gate voltage is swept. Note that the double transition is an evidence of strong exchange coupling ($J \gg T_K^0 \gg \Delta$): for examples, with $T_K^0 \sim 3$K measured in a recent C_{60} single-molecular transistor [24], one estimates $J \sim 30$K. Asymmetry of the phase diagram enables the sign and possibly the amplitude of J to be determined without ambiguity by observing the evolution of the SPR or the critical current.

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